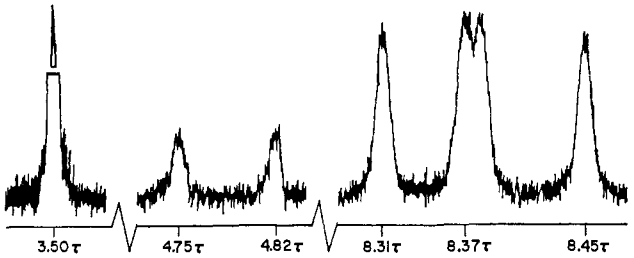
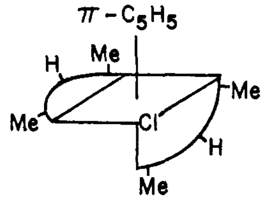
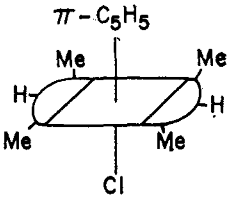


Figure 1. Proton nmr spectrum of (π-C_5H_5)Zr(acac)$_2$Cl in benzene solution at 36° (60 MHz); concentration is 7.5 g/100 ml of solvent.

one stereochemical position and the chlorine atom at a position *cis* to the ring (I). It may be noted that a



I



II

trans configuration such as II, which would have *apparent* C_{2v} symmetry in presence of rapid rotation of the C_5H_5 ring, cannot be present in an appreciable amount, as judged from the relative intensity data. Configurations somewhat similar to I may be derived from a D_{2d} dodecahedron and a D_{4d} square antiprism. In these higher polyhedra (Figure 2) it is assumed that the ring occupies a triangular face in forming three π bonds to zirconium. In the case of the dodecahedron, for example, the C_5H_5 ring may occupy an AAB face with the two acetylacetonate ligands spanning a g–g pair of edges and the chlorine atom at a B position. An analogous antiprismatic configuration may be readily visualized with the acetylacetonates spanning an s–s pair of edges. An X-ray diffraction structure determination on a single crystal by Stezowski and Eick[12] has shown that the stereochemistry more nearly approximates a dodecahedron than an antiprism or an "octahedron." In view of this result, one might have hoped to observe more than one stereoisomer in solution because at least five potentially detectable stereoisomers are possible based on a dodecahedron. Seven additional isomers are possible if the C_5H_5 ring is capable of bonding through an ABB triangular face. Four stereoisomers are possible based on an antiprism. However, no isomerization could be detected after the compound had been heated in benzene solution at 80° for 24 hr. At least four isomers are observed in solution for the benzoylacetonate[13] derivative, (π-C_5H_5)Zr(bzac)$_2$Cl, but, because the diketonate ligand is asymmetric, four geometric isomers can result from a single stereochemical configuration, such as the dodecahedral g–g, B stereoisomer described above.[14]

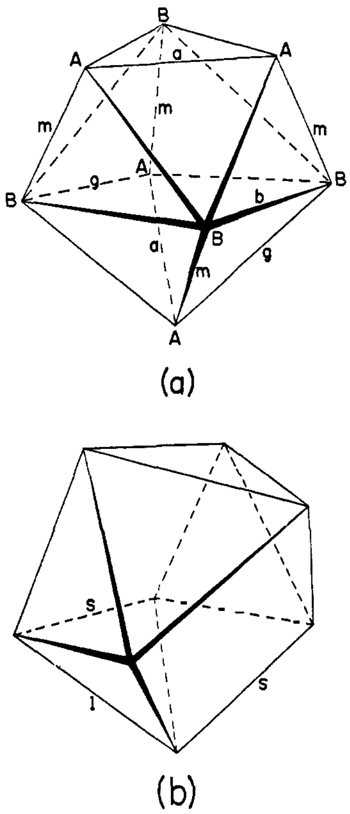


Figure 2. The D_{2d} dodecahedron (a) and D_{4d} square antiprism (b). Edge and vertex notation is from J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 2, 235 (1963).

The ability of the C_5H_5 ring to influence drastically the stereochemical rigidity, or nonrigidity, of the Zr(acac)$_2$Cl moiety is rather remarkable. Variable-temperature nmr experiments are in progress to investigate this phenomenon.

Acknowledgment. We wish to acknowledge support by Michigan State University through All-University Research Funds, Project No. 5392.

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[12] J. J. Stezowski and H. A. Eick, Michigan State University, personal communication, 1968.

[13] $C_6H_5COCHCOCH_3^-$; abbreviation, bzac.

[14] E. D. Butler and T. J. Pinnavaia, unpublished results.

[15] National Defense Education Act Predoctoral Fellow, 1967–1968.

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Received July 10, 1968

Ammonium Ion Determination and Acid–Base Titrations in Liquid Ammonia Using a Glass Electrode

Sir:

The glass membranes of ordinary pH-sensitive glass electrodes show essentially infinite resistance and consequently no detectable sensitivity toward ammonium ion concentration when used in cells having liquid ammonia solutions.[1] However, we have observed that a commercial cationic glass electrode,[2] sensitive in varying degrees to Na^+, H_3O^+, K^+, NH_4^+, Ag^+, and Li^+, can be used to follow ammonium ion concentration in liquid ammonia solutions. In order to permit the use of the electrode in boiling liquid ammonia solutions contained in dewar vessels (−33°), we replaced the dilute aqueous HCl electrolyte in the inner part of the electrode with aqueous

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[1] A. H. A. Heyn and M. J. Bergin, *J. Am. Chem. Soc.*, 75, 5120 (1953).

[2] Beckman Instruments, Inc., Fullerton, Calif., Cationic Electrode No. 39137; see Beckman Bulletin 7017-a and Instructions 1154B.

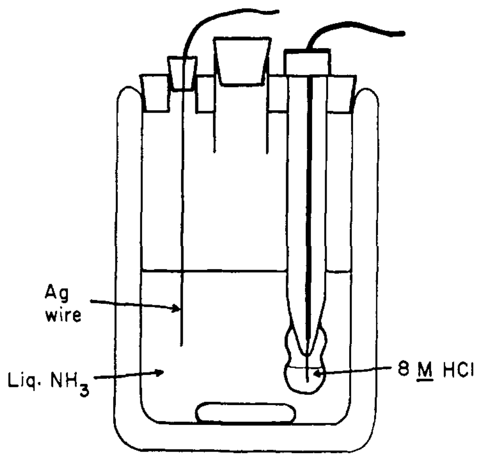

Figure 1. Experimental setup for using a cationic glass electrode in magnetically stirred liquid ammonia solutions in an unsilvered dewar.

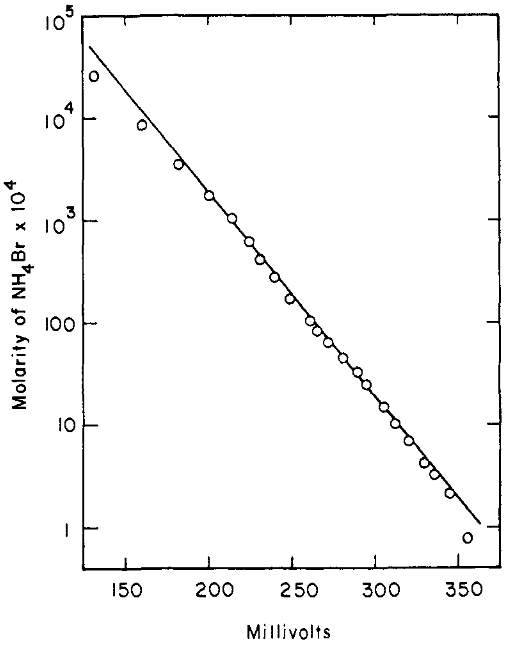

Figure 2. Plot of logarithm of ammonium bromide concentration *vs.* millivolts.

8 *M* HCl saturated with AgCl. The latter solution does not freeze even at the freezing point of ammonia (−77°). As a reference electrode, we used a Ag, Ag^+ electrode, either with or without liquid junction. A liquid junction was required when titrating basic solutions incompatible with the silver ion; in such cases the Ag, Ag^+ couple was contained in a glass cylinder having an asbestos-plugged capillary hole (obtained by disassembling a calomel reference electrode of the type commonly used with pH meters). Potentials were measured using a Radiometer pH meter (Copenhagen, Denmark).

In one series of measurements, the potential of the cell without liquid junction was determined as a function of the ammonium ion concentration. The cell may be represented as Ag, AgCl, 8 *M* HCl (aq), glass membrane, ammonia solution (varying molarity of NH_4Br; 0.001 *M* $AgNO_3$), Ag. The experimental setup is shown in Figure 1, and the data are plotted in Figure 2.

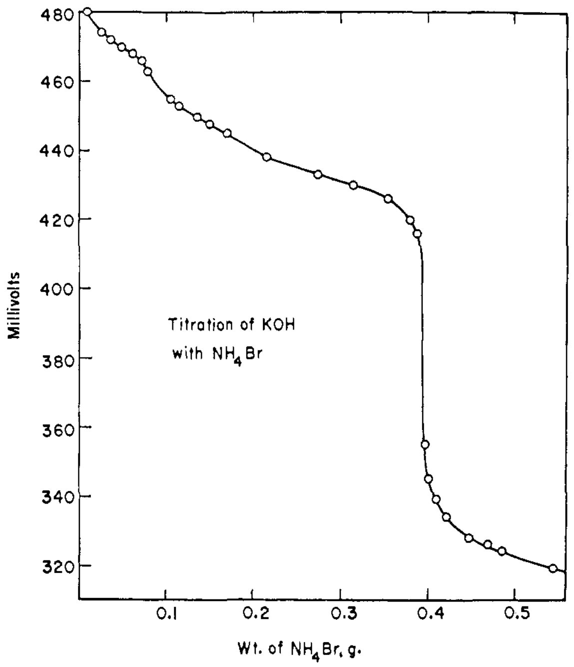

Figure 3. Plot of millivolts *vs.* weight of ammonium bromide added to a suspension of KOH.

The slope of the line drawn through the points in Figure 2 corresponds to 50 mV per decade change in concentration, as compared with the value 48 mV per decade calculated from the Nernst equation. The lowest-concentration point of Figure 2 (for 8×10^{-4} *M* NH_4Br) corresponds to an emf significantly lower than that predicted by the line. This deviation is probably attributable to the presence in the solution of silver ions (10^{-3} *M*), to which the electrode is sensitive.[3,4] The high-concentration points similarly deviate from the line of Figure 2. These deviations can possibly be explained by the trend in the activity coefficient of ammonium bromide in this concentration region.[5]

In another series of measurements, the potential of the cell with liquid junction was followed as weighed amounts of ammonium bromide were added to solutions of potassium amide[7] or suspensions of potassium hydroxide.[8] The cell may be represented as Ag, AgCl,

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(3) The potential of a cation-sensitive electrode (containing a constant internal reference solution) in a solution containing both NH_4^+ and Ag^+ ions can be expressed by the relation $E° = \text{constant} + (nRT/F) \ln (a_{NH_4} + Ka_{Ag})$, where a_{NH_4} and a_{Ag} are the activities of the ammonium ion and silver ion, respectively, *K* is the sensitivity of the electrode toward Ag^+ ions (relative to NH_4^+ ions), and the other symbols have their usual significance.[4] The lower points of the curve in Figure 2 may be closely represented by the expression

$$E(\text{mV}) = 163 - 50 \log (M_{NH_4} + 5 \times 10^{-5})$$

(4) G. Eisenman in "Glass Electrodes for Hydrogen and Other Cations," G. Eisenman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, Chapter 9.

(5) No activity coefficient data for ammonium bromide in ammonia at a temperature near −33° are available. However, activity coefficient data at other temperatures for other uni-univalent salts,[6] when plotted against concentration, show marked upward-tending *curvature* commencing near 1 *M*, resulting in minima at still higher concentrations.

(6) See, for example, the data in J. Jander, "Anorganische und Allgemeine Chemie in flüssigem Ammoniak," Vol. 1, Part 1 of "Chemistry in Nonaqueous Ionizing Solvents," G. Jander, H. Spandau, and C. C. Addison, Ed., Interscience Publishers, New York, N. Y., 1966, pp 42–43, 196–197.

(7) Prepared from a potassium-ammonia solution, using iron(III) nitrate catalyst.

(8) Prepared as a flocculent suspension by adding an excess of water to a potassium-ammonia solution.

8 *M* HCl (aq), glass membrane, ammonia solution (varying NH_4^+ concentration during "titration"), asbestos-plugged capillary junction, ammonia solution (0.001 *M* $AgNO_3$, *ca.* 0.2 *M* KNO_3), Ag. A plot of emf *vs.* weight of added ammonium bromide for a "titration" of a KOH suspension is shown in Figure 3. The sharp inflection point corresponds to the point where the cloudiness due to KOH just disappeared, and the titer agrees within experimental error with that calculated from the weight of potassium converted to KOH. A curve of essentially the same shape was obtained for the titration of a solution of potassium amide with ammonium bromide. When a mixture of potassium hydroxide and potassium amide[9] was titrated, two distinct inflection points were observed, corresponding to the two different end points.

In view of the simplicity of the apparatus, the rapidity with which measurements can be made (electrode equilibrium was usually established within 20 sec), and the results described above, the use of cationic glass electrodes appears to be a promising method for measuring pH values in liquid ammonia. Clearly the method will facilitate end-point determination for acid–base titrations in ammonia. It is hoped that it will permit the determination of absolute p*K* values for acids in ammonia. It will be interesting to apply cationic glass electrodes to the determination of alkali metal ion concentrations (for example, in metal–ammonia solutions).

Acknowledgment. This work was supported by the U. S. Atomic Energy Commission.

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[9] Prepared by adding a small amount of water to a potassium amide solution.

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Received May 25, 1968

The Synthesis of the $W_2Br_9^{3-}$ Ion

Sir:

Although $K_3W_2Br_9$ was described by Young in 1932,[1] no further mention of this compound or its reactions has appeared. Our own efforts to duplicate the synthesis briefly described by Young have resulted in insignificant yields of the desired compound. An alternate synthesis of $W_2Br_9^{3-}$ was provided by a consideration of the kinetic results of Hawkins and Garner,[2] who examined the exchange of radiochloride ion with $W_2Cl_9^{3-}$ in acid solution. Although the chlorine atoms in the dinuclear ion are not structurally equivalent, they were found to be kinetically equivalent. Guided by these results, we examined the simple halogen exchange reaction

$$W_2Cl_9^{3-} + 9Br^- \rightleftharpoons W_2Br_9^{3-} + 9Cl^-$$

in acid solution.

$K_3W_2Cl_9$ was dissolved in a saturated HBr solution at 0°. Samples were withdrawn periodically and insoluble $Rb_3W_2Cl_{9-x}Br_x$ was precipitated by the addition of RbBr. Equilibrium was attained after about 3 hr, whereupon the average composition[3] was $Rb_3W_2Cl_{0.9}Br_{8.1}$, as shown in Figure 1. However, when a moderate flow of gaseous HBr was maintained throughout the course of the reaction, complete exchange occurred within 24 hr. For synthetic purposes the reaction was conveniently performed at room temperature for an equal length of time. *Anal.* Calcd for $Rb_3W_2Br_9$: W, 27.37; Br, 53.54. Found: W, 27.6, 27.4; Br, 53.9, 53.7. Nearly quantitative yields were achieved. The magnetic moment was found to be 0.4 BM, which is identical with the magnetic moment of $Cs_3W_2Cl_9$. The paramagnetism of the latter was recently found[4] to be completely independent of temperature.

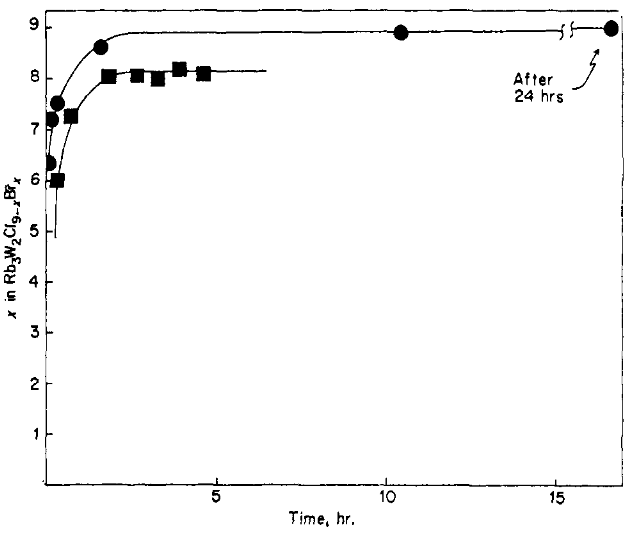

Figure 1. Rates of formation of $W_2Cl_{9-x}Br_x^{3-}$: ■, in a saturated HBr solution, and ●, in a saturated HBr solution with a continuous, moderate flow of gaseous HBr, at 0°.

$K_3W_2Br_9$ can be prepared as brown, hexagonal plates by similar methods but with lower yields due to its higher solubility. In agreement with Young,[1] we find that aqueous solutions of this compound, in the absence of air, are brown when concentrated, but appear orange to pink upon dilution. In the presence of air aqueous solutions are almost immediately decomposed. The spectrum of the compound in dilute HBr solution (Figure 2) is similar to that of $K_3W_2Cl_9$. The lattice constants for the hexagonal unit cell were found from X-ray powder photographs (Cu Kα radiation) to be $a = 7.6$ Å and $c = 17.5$ Å. For $K_3W_2Cl_9$,[5] $a = 7.17$ Å and $c = 16.25$ Å.

A mechanism for the formation of $W_2Br_9^{3-}$ from $W_2Cl_9^{3-}$ remains in some doubt. To account for the equivalent exchange of the chlorine atoms in $W_2Cl_9^{3-}$, Hawkins and Garner[2] considered two possibilities. In the first, the kinetic equivalence could result from an intramolecular exchange of the chlorine atoms in the dinuclear ion concurrent with the exchange with free chloride ion. This possibility was discounted because,

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[1] R. C. Young, *J. Am. Chem. Soc.*, **54**, 4515 (1932). Young describes his synthesis as similar to that used for $K_3W_2Cl_9$, *i.e.*, the reduction of W(VI) with Sn in HCl solutions.

[2] G. L. Hawkins and C. S. Garner, *ibid.*, **80**, 2946 (1958). The order of the reaction with respect to Cl^- was not obtained because of the high concentrations of HCl present in solution.

[3] The samples were decomposed in dilute basic peroxide solutions. Following acidification, Cl^- and Br^- were determined potentiometrically with $AgNO_3$. From synthetic mixtures of these ions, it was determined that both ions could be determined simultaneously up to compositions corresponding to $W_2Cl_{0.5}Br_{8.5}^{3-}$. Beyond this composition, Cl^- could only be obtained by difference.

[4] R. Saillant and R. A. D. Wentworth, *Inorg. Chem.*, 7, 1606 (1968).

[5] W. H. Watson and J. Waser, *Acta Cryst.*, **11**, 689 (1958).